The importance of the chemistry of metal complexes and organometallic compounds towards new synthetic routes, especially the reactions of coordinated ligands, complex mediated reactions and organic conversions influenced by metal or metal complexes has been briefly reviewed in Chapter-I of the present dissertation. The reactivity of macrocycles has also been briefly discussed. Involvements of hydrazines, hydrazones, Schiff bases and cyclopentadienyl ring containing ligands in the newer syntheses have also been discussed in Chapter-I. A very short coverage has also been made on the importance of metal complexes in biochemistry, followed by the Introduction and Scope & Object of the present investigation.

Chapter-II describes the experimental details in general and the preparation of the ligands and some starting materials.

Chapter-III includes lithiation, trimethylsilylation of N,N'-ethylene bis{(3-carboxy)salicylideneiminato}nickel(II)/palladium(II) and their subsequent treatment with CICH₂COOH, CICH₂CH=CH₂, CICH₂OC₆H₅ and CICH₂SC₆H₅ leading to the corresponding new complex derivatives. These, on hydrolyses and normal work-up afforded trisubstituted benzene derivatives [H₂(cm)fsa] (5), [H(allyl)fsa] (6), [H(phm)fsa] (7) and [H(thphm)fsa] (8). The compounds isolated are shown in the schemes I and II.

The complex [Ni(H₂fsaen)] on treatment with SOCl₂ afforded corresponding acid chloride, which on treatment with different amines and subsequent hydrolysis afforded novel derivatives of 3-formylsalicylic acid. Friedel-Crafts acylation of benzene by the above acid chloride has also been successfully achieved, which again on hydrolysis yielded (3-formyl-2-hydroxy)benzophenone, [Hbzphfsa] (11), the novel precursor for macrocyclic ligands. The above reactions are shown in scheme III.
SCHEME I

\[
\text{Ni} \quad \text{H} \quad \text{C} \quad \text{N} \quad \text{O} \quad \text{O} \quad \text{C-OSiMe}_3(\text{Li})
\]

\[
\text{CH}_2 - \text{N} \quad \text{O} \quad \text{O} \quad \text{C-OSiMe}_3(\text{Li})
\]

\[
\text{R}_1 \text{Cl}
\]

\[
(-2\text{Me}_3\text{SiCl})\text{or}(-2\text{LiCl})
\]

\[
\text{SCHEME II}
\]

\[
\text{Ni} \quad \text{H} \quad \text{C} \quad \text{N} \quad \text{O} \quad \text{O} \quad \text{C-OR}_1
\]

\[
\text{CH}_2 - \text{N} \quad \text{O} \quad \text{O} \quad \text{C-OR}_1
\]

\[
(1), R_1 = -\text{CH}_2\text{COOH}
(2), R_1 = -\text{CH}_2\text{CH}=\text{CH}_2
(3), R_1 = -\text{CH}_2\text{OC}_6\text{H}_5
(4), R_1 = -\text{CH}_2\text{SC}_6\text{H}_5
\]

\[
(\text{i}) \text{HCl, ice-water, pH} \approx 5
\]

\[
(\text{ii}) \text{Extracted with CHCl}_3
\]

\[
(5), R_1 = -\text{CH}_2\text{COOH}
(6), R_1 = -\text{CH}_2\text{CH}=\text{CH}_2
(7), R_1 = -\text{CH}_2\text{OC}_6\text{H}_5
(8), R_1 = -\text{CH}_2\text{SC}_6\text{H}_5
\]
SCHEME III

\[
\begin{align*}
(10) & \xrightarrow{\text{In situ Friedel-Crafts Acylation of } C_6H_6 \text{ by (9)}} \\
& \xrightarrow{\text{Acid Hydrolysis at } 0°C} \\
& \xrightarrow{(i) R - \text{NH}_2, (iii) CHCl_3 \text{ extract}} \\
& \xrightarrow{(i) \text{HCl, ice-H}_2\text{O}, (ii) CHCl_3 \text{ extract}} \\
& \xrightarrow{(12), R = C_6H_5CH_2-, (13), R = pCH_3O\text{C}_6\text{H}_4-, (14), R = pCH_3\text{C}_6\text{H}_4-}
\end{align*}
\]
This chapter also includes the reactions of newly synthesized [Hbzphfsa] (11) with H₂NCH₂CH₂NH₂, H₂NCH₂CH₂CH₂NH₂ and

**Scheme IV**

\[
\text{Ph} \quad \text{C=O} \quad \text{H₂N—CH₂} \\
\text{C=O} \quad \text{H₂N—CH₂} \quad \text{MeOH; Reflux}
\]

\[
\text{CuCl}_2 \cdot 2\text{H₂O/MeOH} \quad \text{NiCl}_2 \cdot 6\text{H₂O/MeOH} \\
\text{Zn(OAc)}_2 \cdot 2\text{H₂O} \quad \text{ZnCl}_2; \text{MeOH}
\]

\[
\text{M} \quad \text{Cu} \quad \text{Cu} \quad \text{Cu} \quad \text{Ni} \quad \text{Zn} \\
\text{n} \quad 2 \quad 1 \quad 0 \quad 2 \quad 2
\]

**Compound:** (15) (16) (17) (18) (19)

\[
\text{(20)} : \text{M = Zn, } X = \text{OC(O)CH₃, } n = 1 \\
\text{(21)} : \text{M = Pb, } X = \text{NCS}, \ n = 2
\]

**Scheme V**
H$_2$NCH$_2$CH(OH)CH$_2$NH$_2$ in the presence of different metal salts in varied reaction conditions yielding new macrocyclic metal complexes, (15) to (23) and are shown in the schemes IV to VI.

**SCHEME VI**
Chapter-IV (Section 4.1) describes the syntheses of two new organometallic ligands, namely 1-formylferrocene morpholine N-thiohydrazone (HFfmth) and 1-acetylferrocene morpholine N-thiohydrazone (HAfmth) (Scheme VII) and their reactions with nickel(II), cobalt(II), copper(II), zinc(II) and cadmium(II) salts leading to the isolation of complexes of the types ML_2 and ML_3 (where HL = HFfmth or HAfmth) and are shown in scheme VIII.

SCHEME VII

\[
\begin{align*}
\begin{array}{c}
\text{Fe} \quad \text{R} \quad \text{C}=\text{O} \\
\text{H}_2\text{NNH-C} \quad \text{S} \\
\text{Fe}
\end{array}
\end{align*}
\]

\[
\begin{align*}
\text{R} = \text{H/CH}_3 \\
\text{HFfmth, where R = H} \\
\text{HAfmth, where R = CH}_3
\end{align*}
\]

This section also includes the interactions of the ligand HFfmth with Me_2SnCl_2, MeSnCl_3 and (t-Cp)_2TiCl_2 in varied reaction conditions yielding a new series of organotin(IV) and organotitanium(IV) compounds which are shown in scheme IX.
SCHEME VIII

\[ \text{M(OAc)}_{2n}\text{H}_2\text{O} \rightarrow \text{pH} \sim 6 \]

\[ \begin{align*}
\text{MC}^n\text{H}^n \text{OR} & \quad \text{M} < \text{Ni} \quad \text{Ni} \quad \text{Cu} \quad \text{Cu} \quad \text{Zn} \quad \text{Zn} \quad \text{Cd} \quad \text{Cd} \\
\text{Complex No.} & \quad (1) \quad (2) \quad (5) \quad (6) \quad (7) \quad (8) \quad (9) \quad (10)
\end{align*} \]

\[ \begin{align*}
\text{R} & \rightarrow \text{H} \quad \text{CH}_3 \quad \text{H} \quad \text{CH}_3 \quad \text{H} \quad \text{CH}_3 \quad \text{H} \quad \text{CH}_3 \\
\text{M} & \rightarrow \text{Ni} \quad \text{Ni} \quad \text{Cu} \quad \text{Cu} \quad \text{Zn} \quad \text{Zn} \quad \text{Cd} \quad \text{Cd}
\end{align*} \]

\[ \begin{align*}
\text{R} = \text{H}, \text{Hffmth} & \\
\text{R} = \text{CH}_3, \text{Hffmth}
\end{align*} \]

\[ \text{Co(OAc)}_2 4\text{H}_2\text{O} \rightarrow \text{EtOH, NH}_4\text{OH} / \text{O}_2 \]

\[ \begin{align*}
\text{R} & \rightarrow \text{H}, (3) \\
\text{R} & = \text{CH}_3, (4)
\end{align*} \]
SCHEME IX

\[
\text{Me}_2\text{SnCl}_2 \xrightarrow{\text{MeOH - MeNO}_2 \text{ Reflux}} \text{Me} \text{SnMe} \\
\]

\[
(11)/(12)
\]

\[
\text{MeSnCl}_3 \xrightarrow{\text{MeOH - MeNO}_2 \text{ Reflux}} \text{Me} \text{SnCl} \\
\]

\[
(13)/(14)
\]

\[
(\kappa-\text{Cp})_2\text{TiCl}_2 \xrightarrow{\text{DRY EtOH, Reflux}} \text{Ti} \\
\]

\[
(15)
\]

where, \(\text{SN} \) = Anion of monobasic bidentate ligand, HFFmth or HAFmth
Lastly this section describes the reactions of newly synthesized compound MeSn(Ffmth)$_2$Cl (13) towards MeSH, Me$_2$NSiMe$_3$, Me$_3$Si(N$_3$) and Me$_3$SiC≡C-Ph leading to many new organotin(IV) derivatives by the cleavage of 'Sn-Cl' bond (Scheme X).

**Scheme X**

![Scheme X](image)

$L_1=$ SMe, (16)  
$L_1= -$ NMe$_2$, (17)  
$L_1= -$ N$_3$, (18)  
$L_1= -$ C≡C-Ph , (19)

where $\left(\begin{array}{c} S \\ N \end{array}\right)$ = Anion of monobasic bidentate ligand, HFFmth

Section 4.2 of Chapter-IV describes the isolation of two new ferrocenyl hydrazones, namely 1-formylferrocenyl 4-methoxybenzoyl hydrazone (HFFmBH) and 1-acetylfenrcenyl 4-methoxybenzoyl hydrazone (HAgmBH) (Scheme XI) and also their reactions with metal salts and organometal salts leading to the formation of many new metal complexes including organotin(IV) and organotitanium(IV) complexes (Schemes XII XlV) of these ligands.
**SCHEME XI**

R = H, CH₃

\[
\text{Fe} \quad + \quad \text{H₂NNH-C-}\text{O-OCH₃} \quad \xrightarrow{\text{EtOH}} \quad \text{Fe} \quad \text{H₂SO₄} \quad \text{Reflux} \quad \text{R = H, CH₃} 
\]

**SCHEME XII**

R = H, HFfmbh

R = CH₃, HAFmhbh

\[
\text{Fe} \quad \xrightarrow{\text{NiCl₂6H₂O; EtOH}} \quad \text{Fe} \quad \text{N} \quad \text{C} \quad \text{N} \quad \text{O} \quad \text{OCH₃} \quad \text{R = H, CH₃} 
\]

\[
\text{Fe} \quad \xrightarrow{\text{CuCl₂2H₂O; EtOH}} \quad \text{Co(OAc)₂2H₂O, EtOH; Reflux} \quad \text{Fe} \quad \text{N} \quad \text{C} \quad \text{N} \quad \text{O} \quad \text{OCH₃} \quad \text{R = H, CH₃} 
\]

<table>
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<th>Ni</th>
<th>Cu</th>
<th>Cu</th>
<th>Zn</th>
<th>Zn</th>
<th>Cd</th>
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<td>0</td>
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<td>0</td>
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</tr>
</tbody>
</table>

Complex No: (1) (2) (3) (4) (5) (6) (7) (8) (9) (10)
SCHEME XIII

\[
\begin{align*}
(\alpha-Cp)_{2}TiCl_{2} & \quad \text{DRY CHCl}_{3} \quad \text{REFLUX} \\
(\alpha-Cp)_{2}TiCl_{2} & \quad \text{Et}_{3}N; \text{DRY CHCl}_{3} \quad \text{Stirred}
\end{align*}
\]

R = H, HFfmbh
R = CH₃, HAtfmbh

SCHEME XIV

\[
\begin{align*}
\text{Me}_{2}SnCl_{2} & \quad \text{MeOH–MeNO}_{2} \quad \text{Reflux} \\
\text{MeSnCl}_{3} & \quad \text{MeOH–MeNO}_{2} \quad \text{Reflux}
\end{align*}
\]

R = H, HFfmbh
R = CH₃, HAtfmbh

(13), R = H, X = CH₃
(14), R = CH₃, X = CH₃
(15), R = H, X = Cl
(16), R = CH₃, X = Cl
Chapter-V finally describes the syntheses and characterization of some new ferrocenyl Schiff bases (Scheme XVI) and their complexes with copper(II), cobalt(II) and nickel(II) of the type $[M(L)(X)(NH_3)]$ where, HL = stands for monobasic bidentate ferrocenyl Schiff bases and $X = OH$ or $Cl$, and cobalt(III) complexes, $[Co^{III}(L)_2(OH)(NH_3)]$ as shown in the (Schemes XVII to XX).
SCHEME XVII

\[
\text{Fe} \quad \text{C}=\text{O} \quad \text{H}_2\text{N} - \text{R}'
\]

\[
\text{Fe} \quad \text{C}=\text{N} - \text{R}'
\]

\[
\text{MeOH OR CHCl}_3 \quad \text{REFLUX} \quad \text{Acetic Acid OR Pet.ether}
\]

\[
\text{R = H / CH}_3
\]

HAfaa; when \( R = \text{H} \) and \( R' = -(CH_3)_2\text{C}=\text{H}_2 - \text{NH}_2 \)

HFfap; when \( R = \text{H} \) and \( R' = -\text{CH}_3\text{C}=\text{H}_2 - \text{OH} \)

HAfap; when \( R = \text{H} \) and \( R' = -\text{CH}_3\text{C}=\text{H}_2 - \text{NH}_2 \)

HFfaba; when \( R = \text{H} \) and \( R' = -\text{CH}_3\text{C}=\text{H}_2 - \text{COOH} \)

HAfaba; when \( R = \text{CH}_3 \) and \( R' = -\text{CH}_3\text{C}=\text{H}_2 - \text{COOH} \)

SCHEME XVII

\[
\text{Fe} \quad \text{C}=\text{N} \quad \text{H}_2\text{N}
\]

\[
\text{Fe} \quad \text{C}=\text{N} \quad \text{NH}
\]

\[
\text{MCl}_2\text{nH}_2\text{O OR M(OAc)}_2\text{nH}_2\text{O ETOH; pH~7}
\]

\[
\text{R = H , HFfaa}
\]

\[
\text{R = CH}_3, \text{HAfaa}
\]

\[
\text{Complex No} \quad (1) \quad (2) \quad (3) \quad (4) \quad (5) \quad (6) \quad (7) \quad (8)
\]

\[
\text{M} \rightarrow \text{Ni} \quad \text{Ni} \quad \text{Co} \quad \text{Co} \quad \text{Cu} \quad \text{Cu}
\]

\[
\text{R} \rightarrow \text{H} \quad \text{CH}_3 \quad \text{H} \quad \text{CH}_3 \quad \text{H} \quad \text{CH}_3
\]

\[
\text{n} \rightarrow 2 \quad 2 \quad 0 \quad 0 \quad 0 \quad 0
\]
SCHEME XVIII

\[
\text{Cu(OAc)}_2 \cdot \text{H}_2\text{O} \rightarrow \text{NH}_4\text{OH, EtOH; pH} \approx 9
\]

R = H, HFtaa
R = CH₃, HAtaa

R = H, (5); R = CH₃, (6)
SCHEME XIX

\[ \text{NiCl}_2 \cdot 6\text{H}_2\text{O} ; \text{NH}_4\text{OH} (\text{aq}) \]

\[ \text{EtOH OR} \]

\[ \text{CoCl}_2 \cdot 6\text{H}_2\text{O} ; \text{EtOH} \]

\[ \text{NH}_4\text{OH} / \text{Na.pH}^\circ \text{Q} \]

\[ \text{Ni(OAc)}_2 \cdot 4\text{H}_2\text{O} \]

\[ \text{OR} \]

\[ \text{Cu(OAc)}_2 \cdot 2\text{H}_2\text{O} \]

\[ \text{NH}_4\text{OH} (\text{aq}) \]

\[ \text{EtOH, pH} \sim 9 \]

\[ \text{M} \rightarrow \text{Ni} \]

\[ \text{R} \rightarrow \text{H} \]

\[ \text{Comp. No: (10) (12) (14)} \]

HFtap, R = H

HAfap, R = CH₃

\[ \text{M} = \text{Ni}, (11) \]

\[ \text{M} = \text{Cu}, (15) \]

\[ \text{Co(OAc)}_2 \cdot 4\text{H}_2\text{O} \]

\[ \text{NH}_4\text{OH} / \text{O}_2; \text{EtOH} \]

\[ \text{pH} \sim 9 \]

(13)
All the compounds isolated have been characterized with the help of elemental analyses, molar conductances, magnetic susceptibility data, molecular weights and spectroscopic data (uv-visible, i.r., $^1$H n.m.r.).

Finally, the concluding remarks have been recorded and the new possibilities have been envisaged on the basis of the present findings.